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Weight of Hydrogen.

By William A. Noyes.

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THE CHOICE OF THE MOST PROBABLE VALUE FOR AN ATOMIC WEIGHT: THE ATOMIC WEIGHT OF HYDROGEN.¹

BY WILLIAM A. NOYES.

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A large amount of material has been accumulated from which the atomic weights of the more important elements can be calculated. A very superficial examination of this material reveals the fact that the experimental results on which our knowledge of these constants is based, vary very greatly in their value and that many of the older determinations have been rendered practically worthless by recent work, which has been more careful and accurate.

As some of these new determinations affect the values for elements of such fundamental importance that a recalculation of the whole table of atomic weights will be necessary in the near future, it seems desirable to formulate some general principles to aid in the elimination of results which have little or no value and in the combination of the results which remain. Such principles, if they meet with general acceptance, will be of value, not only for the purpose stated but also as setting a certain standard which must be attained by future workers in this field, if their work is to be of permanent value.

The most important general principle which has been proposed for the combination of the results of different observers, is the one based on the mathematical discussion of accidental errors of observation. In accordance with the theory of probabilities, these results, if subject only to accidental errors, should be weighted in inverse proportion to their

¹ Presented in abstract at the N. Y. Meeting of the American Chemical Society, Dec. 28, 1906.

probable errors.¹ A very serious objection to this method of treatment lies in the fact that every determination of this kind is subject to constant errors, and that the amount of these errors is not proportional to their "probable errors."² Thus Stas obtained 132.8445 ± 0.0008 parts of silver chloride from 100 parts of silver, while Richards and Wells³ have obtained 132.8670 ± 0.0005 parts. The most probable value calculated by the mathematical rule would be 132.8607. If this value is the true one, the real error of the value obtained by Richards and Wells is 12 times its probable error, while the real error of Stas is 20 times the probable error. And, whatever the true value may be, the real error of one of the results, at least, is many times its "probable error." An examination of other cases shows that the relations here found are typical, and it seems evident that the question of constant errors requires some other treatment than the simple mathematical one. The proper treatment, which is an experimental one, has been clearly illustrated in the case which we have under consideration. Richards and Wells studied their method very carefully with especial reference to the elimination of constant errors and to secure evidence as to the amount of those errors which could not be wholly excluded. They also pointed out certain errors in the work of Stas and determined, approximately, the magnitude of some of these. It is evident for this reason that very much greater weight attaches to the value found by Richards and Wells than to that found by Stas, and it is proposed as a general principle that when a later observer has pointed out sources of error which are considerable in comparison with the "probable errors" and where the later observer has succeeded in avoiding these sources of error, the earlier work must be looked upon as having only confirmatory value and the result of the later work should be accepted without modification. It has been objected to this that the later work is also subject to constant errors which may be in the opposite direction from those of the earlier determination and that if we give a certain weight to the earlier work we may eliminate these errors. But we certainly are not justified in using a value that contains a known error in one direction merely for the chance that we may compensate an unknown error.

¹ F. W. Clarke: "Constants of Nature," Part V., Edition of 1897, p. 7.

² Professor Clarke has, of course, recognized the importance of constant errors and has often rejected values which he considers subject to such errors. In 1898 (*Amer. Chem. J.*, 20, 543) Prof. T. W. Richards pointed out the importance of selecting atomic weights on the basis of the methods employed in their determination and the probable freedom of those methods from constant errors. It is interesting to notice that of the seven values in Professor Richards's table, which differed at that time decidedly from the values given by Professor Clarke, the numbers for four of the atomic weights are nearer to the numbers now given in the International table than were the values then given by Professor Clarke.

³ This Journal, 27, 524.

The principle outlined above has been recently proposed, independently, by Professor Guye,¹ in his discussion of the selection of the most probable value for the density of a gas. A second principle proposed by Professor Guye is that when the values obtained by two observers agree while that obtained by a third observer is discordant, the values which are in agreement should be given much greater weight. As an extension of this principle, a value of an individual worker which differs materially from the values obtained by several others, should be rejected entirely.

After eliminating the results which are excluded by the application of the foregoing principles, it is proposed to arrange those which remain in the order of their probable errors. Any result with a probable error more than five times that of the smallest probable error may be excluded, as such a result will have only one twenty-fifth the weight, according to the theory of probabilities. In practical effect, this is the same as using the mathematical rule which Professor Clarke has so long employed in weighting the results of different workers. As at least five or six observations are necessary to give a probable error which has any significance, results based on a smaller number of determinations may be excluded unless other evidence warrants the belief that the work is of an unusual degree of accuracy.

The values for any given ratio which remain after the elimination of results which have little value, may well be combined by weighting them inversely as the squares of their probable errors.

For further use, the ratios which are selected in this manner should be weighted, not by the probable error calculated by the mathematical rule but by the deviation of the results of different observers from the value selected. If the results of only one observer remain after eliminating untrustworthy values (as in the case of the ratio of silver to silver chloride), this result should be weighted in accordance with the average deviation of the results of this observer from his mean. This will, I think, give a much fairer basis than the "probable error" for weighting the value in such cases. Thus the "mean error" of the value of Richards and Wells given above is 0.0018, while the "probable error" is 0.0005. When we consider the certainty that some sources of constant error will always remain, I think every one will agree that the real error is much more likely to correspond to the former than to the latter value.

After selecting the most trustworthy experimental ratios as suggested, we have still to combine them for the calculation of atomic weights. This may usually be done in a variety of ways. In choosing among these, the same general principles as before should be applied. For a given atomic weight, only those ratios should be used for which the un-

¹ Arch. sci. phys. nat., 24, 44.

certainities of the values will affect the atomic weight chosen less than five times as much as any other combination of ratios which might be used. In most cases this will probably lead to the selection of ratios which furnish a direct comparison with oxygen, silver or one of the halogens rather than of those in which the comparison is more indirect. Densities of gases corrected to the condition of an ideal gas by the method of D. Berthelot¹ may be considered as direct comparisons with oxygen, and molecular and atomic weights calculated from these densities should be included with those determined by chemical methods.

The Atomic Weight of Hydrogen.

The following is a summary of the determinations which have been made of the atomic weight of hydrogen by the chemical method:

	Date.	No. of expts.	Value.	Prob. error.	Real error.	Real error Prob. error'
Dulong and Berzelius.....	1821	3	1.00667	356	108	0.3
Leduc.....	1892	2	1.00749	83	26	0.3
Erdmann and Marchand.....	1842	8	1.00160	71	615	8.7
Thomsen.....	1870	8	1.00570	71	205	2.9
Rayleigh.....	1889	5	1.00692	56	85	1.5
Dumas.....	1842	19	1.00250	44	525	12.0
Keiser.....	1898	8	1.00753	31	22	0.7
Dittmar and Henderson....	1890	24	1.00840	29	65	2.2
Noyes (recalculated).....	1890	24	1.00765	17	10	0.6
Thomsen.....	1895	21	1.00826	14	51	3.6
Cooke and Richards.....	1887	16	1.00826	13	51	3.9
Noyes (original).....	1890	24	1.00654	11	121	11.0
Keiser.....	1888	10	1.00306	7	469	67.0
Noyes.....	1907	48	1.00787	2	12	6.0
Morley.....	1895	23	1.00762	2	12	6.0

The probable errors of the table are calculated from those assigned by Professor Clarke.² For the results of Erdmann and Marchand and Leduc, the values are arbitrary. For convenience these errors are given in units corresponding to the last significant figure of the values for the atomic weights.

On applying the principles which have been outlined, we find that the results of Dulong and Berzelius, Erdmann and Marchand, and of Dumas, are excluded because the later work of Dittmar and Henderson by the same method, demonstrates that serious constant errors were involved in the earlier work. Leduc's value is to be rejected because the number of experiments was too small. Keiser's earlier value is to be rejected because it is not in accord with any of the later work and because he has himself given us a later and better value. My own original value must be rejected because it was subject to a constant error and

¹ Compt. rend., 144, 76.

² "Constants of Nature," Part V., p. 24 (1897).

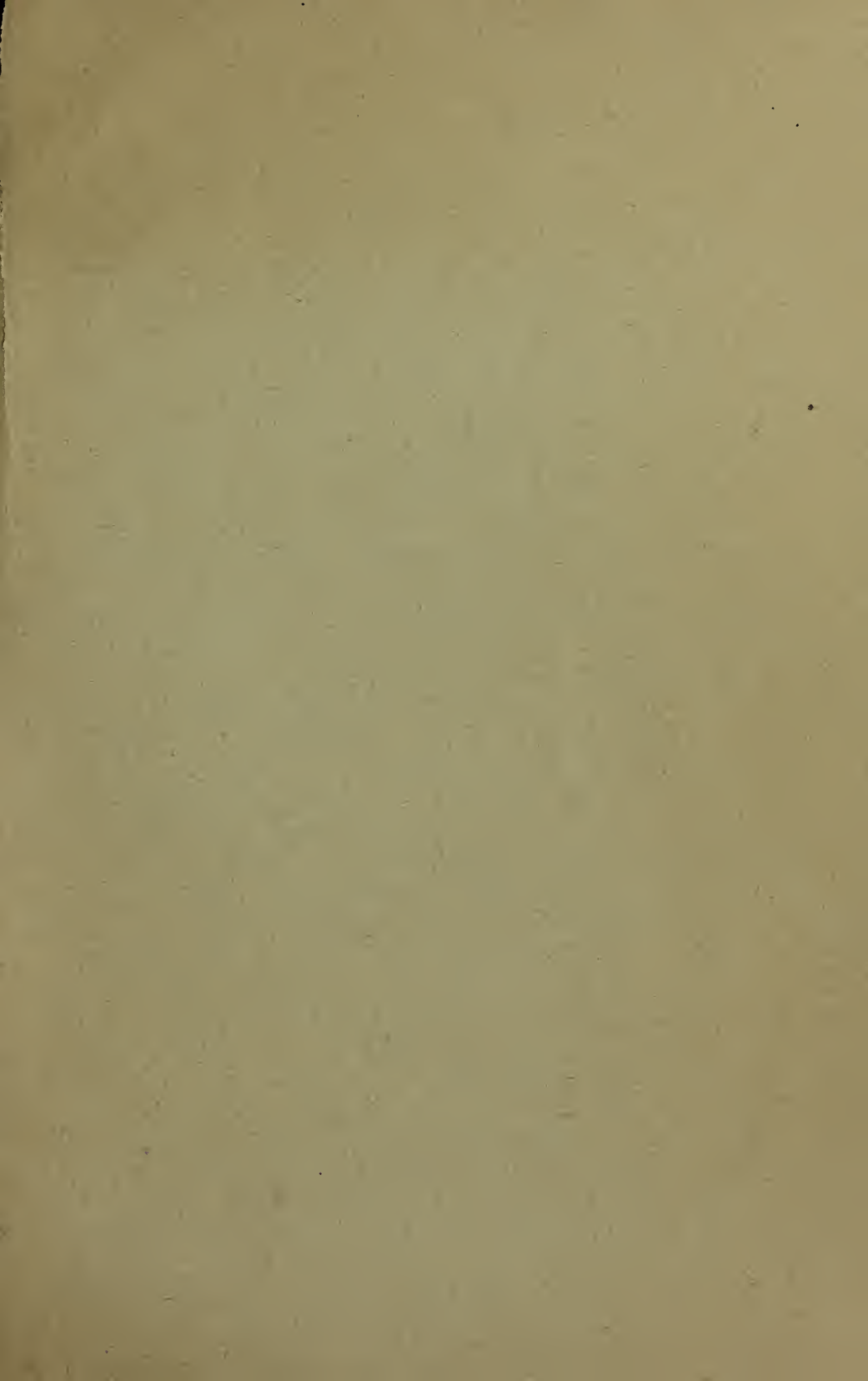
the recalculated result may be considered as superseded by my later and more careful work. Because the probable errors of all of the other determinations are more than five times as great as those of Morley and myself, they would be excluded by the third principle proposed. The final value, if calculated from these two results, is **1.00775**.

It is interesting to notice the relation between the real errors of the various values (assuming this value as true) and the probable errors. *Only in those cases where we now know that there were serious constant errors, is the real error more than six times the probable error.*

Morley calculates a value corresponding to 1.00762 from his determinations of the densities of the gases and their combining volumes. This value has not been considered here, partly because the probable error of the density of hydrogen is about 3 in 100,000, instead of 2 for the chemical method, but chiefly because of the uncertainty of the ratio of the combining volumes.¹

If a value is calculated by Professor Clarke's method, weighting each result in inverse proportion to its probable error, only Keiser's older value and my own original value would affect the value which I have selected by more than about one part in 100,000. Keiser's older value would, however, reduce it by about 40 parts and my own original value by about 4 parts in 100,000.

¹ Morley: "Smithsonian Contribution to Knowledge," No. 980, p. 110 (1895).
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